" On Electric Resistance Thermometry at the Temperature of
Boiling Hydrogen."*   By Professor JAMES DEWAR, M.A.,
LL.D., F.R.S.   Received February 25,—Read March 10, 1904.

[PLATE 10.]

In my paper entitled " The Boiling Point of Liquid Hydrogen
determined by Hydrogen and Helium Gas Thermometers," communi-
cated to the Society in 1901, I detailed means taken to determine the
temperature in gas thermometer degrees at which liquid hydrogen
boils.   The experiments clearly proved that the constant-volume
hydrogen gas thermometer is reliable under varying conditions, down
to a temperature some degrees below the boiling point of hydrogen,
$20°\cdot5$ absolute, on the Centigrade scale.

In the course of making low temperature determinations, a number
of thermometers of different kinds were employed, some being
constant-volume gas thermometers, others in the form of thermo-
electric junctions, and a set depending on change of electric resistance
with temperature.   The group of thermometers depending upon the
assumed relation between electromotive force and temperature broke
down about the temperature of liquid oxygen, while those based upon
the ordinary law correlating change of electric resistance with tempera-
ture failed for all the metals and alloys somewhere above the boiling
point of liquid hydrogen.

In the first experiments made to ascertain the boiling point of
liquid hydrogen under a pressure of 30 to 60 mm. a platinum resist-
ance thermometer was used, with the result that only $1°$ of reduction
of temperature in the boiling point was recorded instead of some
$5°$ indicated by theory.   This result suggested that in all probability
the rate of change of resistance with the pressure became gradually
smaller under very low temperatures.

In the Bakerian Lecture I adverted shortly to some results obtained
in low temperature resistance thermometry, and gave a table† of
numerical values deduced from experimental observations for some of
the more prominent metal resistance thermometers.   In the present
communication the experimental records of eight additional electric
resistance thermometers are given, and the results of the observations
on all the resistance thermometers used during the investigations
are collected and compared.

Two facts seem to result from this inquiry, viz. : (1) That the
resistance of an unalloyed metal continually diminishes with tempera-
ture and in each case appears to approach to a definite asymptotic

* In continuation of Art. 3 of the Bakerian Lecture, ' Roy. Soc. Proc.,' vol. 68,
p. 360.

† ' Roy. Soc. Proc.,' vol. 68, p. 363.

value below which no further lowering of the temperature seems to reduce it; and (2) that the parabolic connection between temperature and resistance is no longer tenable at very low temperatures.

Of the different thermometers constructed on the electric resistance principle, fifteen were serviceable throughout the investigations; the others broke or failed from various causes. The metals employed were platinum, gold, silver, copper, palladium, iron, nickel, and two alloys, platinum-rhodium, and German silver. The metals were supplied by Messrs. Johnson and Matthey, and the late Sir W. C. Roberts-Austen of the Mint. Every endeavour was made to attain the highest purity in the samples. In the Bakerian Lecture a table* was given containing the constants of seven of these thermometers, and in the annexed Table I similar results are given for the remaining eight.

The observed resistances, after all corrections were made, were reduced both by Callendar's and by Dickson's methods, and the close accord of their results is apparent. When these temperatures are compared with the results given by the hydrogen thermometer, they confirm the general inferences above referred to. In the Callendar method the α was determined from the resistances at 100° C. and 0° C., and the δ was then obtained from the resistance and corresponding observed temperature of liquid oxygen boiling under atmospheric pressure. The same data were used in the Dickson formula, except in a few cases where it was thought worth while to employ the method of least squares, in which cases these data were included.

In Table I the suffix number attached to the name of each metal indicates a particular thermometer in my notes of the observations, and may be taken as a rough index of the chronological order in which the observations were made.

Platinum, gold, silver, and copper show a remarkable agreement between the two methods of reduction. The later specimens of the metals of each of these groups are purer than the earlier ones. In the platinum and gold groups we notice that the Centigrade temperature Ω, at which the resistance would vanish, rises with the purity. This is still seen in copper, but something of the reverse appears in the case of silver (perhaps this may be explained later). However, the general rule is again apparent in palladium. With regard to Callendar's coefficients, the temperature coefficient α increases with the purity of the metal, while the difference coefficient δ diminishes; nevertheless some uncertainty is apparent in the platinum thermometer. Alloys appear to have much smaller values of α and much larger values of δ. On the other hand the magnetic metals have greater α's and very much increased δ's.

A marked peculiarity in the magnetic metals is that the difference coefficient δ is negative, that is, the temperatures in metal-degrees

* *Loc. cit.*

Table I.—Electric Resistance Thermometry at the Boiling Point of Liquid Hydrogen.

Metals.	Platinum (P_7).	Gold (Au_{33}).	Silver (Ag_{34}).	Copper (Cu_{37}).	Palladium (Pd_{35}).	Palladium (Pd_{46}).	Nickel (Ni_{41}).	German silver (Arg_{92}).
R_1, ...	7·3519	2·856	4·447	1·623	4·108	9·801	5·567	7·049
R_0, ...	5·3280	2·099	3·209	1·144	3·255	7·261	3·449	6·859
Resistance at CO_2	1·3984	0·729	0·895	0·231	1·485	2·022	—	6·702
„ liq. O	—	—	—	—	—	1·612	0·718	6·466
„ liq. N	—	—	—	—	—	—	—	6·444
„ liq. O, x	0·129	0·234	0·122	0·020	0·893	0·439	0·294	6·407
„ liq. H	0·114	0·219	—	—	—	0·382	—	6·319
„ liq. H, x	—	—	—	—	—	—	—	—
$\alpha = \ldots$	0·003799	0·003607	0·003858	0·004187	0·002621	0·003498	0·006141	0·000277
$\Omega' = -\dfrac{1}{\alpha}$	-263·25	-277·28	-259·21	-238·83	-381·77	-285·87	-162·83	-361·00
T. observed of liq. O	-182°·6 C.	-182°·4 C.	-182°·34 C.	-182°·85 C.	-182°·34 C.	-182°·41 C.	-182°·45 C.	-182°·4 C.
δ	2·2402	-0·27508	0·88769	1·5004	4·6872	4·6298	-10·3836	4·7447
Calculated temp. C.— At CO_2	—	—	—	—	—	—	—	-76°·25 / -78°·94
„ liq. O	-182°·600 / -182°·67	-182°·40 / -182°·5	-182°·345 / -182°·34	-182°·846 / -182°·850	-182°·343 / -182°·340	-182°·410 / -182°·410	-182°·455 / -182°·60	-182°·400 / -184°·35
„ liq. N	—	—	—	—	—	-194°·66 / -194°·39	—	-191°·85 / -193°·47
„ liq. O, x	—	—	—	—	—	—	—	-207°·60 / -208°·54
„ liq. H	-238°·76 / -239°·44	-248°·76 / -249°·87	-242°·01 / -241°·92	-223°·78 / -223°·66	-237°·68 / -235°·75	-232°·73 / -231°·21	-224°·75 / -216°·37	-244°·30 / -243°·00
„ liq. H, x	-239°·42 / -239°·09	-250°·78 / -250°·88	—	—	—	-234°·51 / -232°·91	—	—
Ω	-244°·40 / -244°·02	-280°·22 / -280°·37	-251°·37 / -251°·26	-227°·64 / -227°·50	-316°·99 / -309°·12	-246°·36 / -244°·22	-260°·09 / -240°·65	-1867°·20 / -2325°·21
Ratio $\dfrac{R_0}{\text{Res. at B.P. of H}}$	41·30	8·97	26·30	57·20	3·645	16·54	11·73	1·085

R_1, R_0 are the resistances at 100° C. and 0° C. respectively.

x means that the liquid is boiling under exhaustion measured by about 30 mm. of mercury.

Ω' is the temperature, in degrees of the metal in question, at which the resistance would vanish.

Ω is the temperature Centigrade at which the resistance would vanish, either on the Callendar or on the Dickson method.

Calculated temperatures—the upper by Callendar's method; the lower by Dickson's.

Callendar's α and δ are calculated from the given values of R_1, R_0, the resistance of the metal in liquid O, and the temperature observed in liquid O.

The same data are used to calculate the Dickson formula, except in the cases of P_1, whose formula is given in 'Phil. Mag.,' June, 1898; P_7, whose formula is given in 'Roy. Soc. Proc.,' vol. 64, p. 228, and $Pt\text{-}Rh_{29}$, Arg_{38}, and Cu_{47}, which were calculated by least squares. [For other seven metals, see Table, 'Roy. Soc. Proc.,' vol. 68, p. 363.]

Note.—In the table (vol. 68, p. 363) given in the Bakerian Lecture, the heading of the third column should be "Platinum" P_{27}, not "Potassium" P_{27}.

are algebraically higher than in Centigrade degrees, a peculiarity which is shared with them by gold.   It is also remarkable that in the cases of all the purest metals examined, their resistances calculated by either method of reduction vanish at temperatures above $-273°$ C.   (Au_{33} was not so pure as Au_{40}, which was electrolytic gold.)

As measurers of temperature gold and silver seem to be the best. One prominent characteristic associated with them is, that their δ's are the smallest.   Clearly those metals (if there are any) are accurate temperature measurers for which δ vanishes, so that we expect those to be best in which this constant is least.   There is a further characteristic displayed by the best metals as shown in Table I, which may be explained thus : both methods of reduction rely on the parabola, and the farther away the representative arc of the parabola is from the vertex of the curve, the more nearly straight does this arc become and the smaller will δ be.   Now in both metals referred to, especially in the purer specimens, this characteristic is most marked compared with the other metals employed.*

It is worthy of note that for these pure platinums the average value of δ is very nearly 2·5, while Callendar's platinums, also pure, gave 1·5—1·6.   Is the parabola determined by the resistance at 444°·53 C., 100° C. and 0° C., different from that determined by the resistances at 100° C., 0° C., and $-182°·5$ C. ?   In the sequel I shall show that these must be different, and, in fact, that we must look for an entirely different hypothesis to correlate resistance and temperature.

As a matter of interest, in the last line of Table I, I have noted the ratio in which the resistance of each metal at 0° C. is reduced on cooling it to the boiling point of hydrogen.   This seems to be a quantity showing no connection with other properties of metals.

So far we have looked at the results rather from the point of view of metals as thermometers.   But a much more important question is, What is the relation between resistance and temperature in metals ?

We are entitled to consider the temperatures at which liquid oxygen and hydrogen boil under atmospheric pressure as being known to within one- or two-tenths of a degree, namely, $-182°·5$ C. and $-252°·5$ C.   Further observations made with the constant-volume hydrogen gas thermometer lead to the conclusion that hydrogen

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* In the Callendar parabola $(A-T)^2 = P(B-R)$, the values of A for Au_{40} and Ag_{43} are $-27,053°$ and $14,520°$ (the only other one greater than 10,000° being $-18,087°$ for Au_{33}), and the corresponding values of B are $-598°$ and $177°$ (the only other one greater than 100 being 135° for P_{27}).   Similarly in the Dickson parabola $(a+R)^2 = p(b+T)$ the values of a for Au_{40} and Ag_{43} are $-1080°$ and 339° (the only other two greater than 100 being 251° for P_{27} and $-129°$ for Au_{33}), and the corresponding values of b are $-11,841°$ and 7319° (the only others greater than 2000° being $-8400°$ for Au_{33} and 2881 for Ag_{34}).   This characteristic comes out equally strongly when the curves are reduced to a common resistance of (say) 1000 ohms at 0° C.

freezes about 5° below its boiling point. In the present experiments I have been able to get eight observations in liquid hydrogen boiling under pressures varying from 5—50 mm., and it will not lead us appreciably astray to take the temperatures of these observations as (say) 4° below the boiling point. If the law connecting resistance with temperature be parabolic, the very gentle curvature at the boiling point of hydrogen will allow us to consider the rate of drop in resistance per degree of temperature for the 4° below the boiling point of hydrogen as roughly the same as that between the boiling points of oxygen and hydrogen (70°), so that the ratio of these two drops on this supposition should be about 4 : 70, or say one-eighteenth. These ratios are given in Table II.

Table II.

P_7.	P_{27}.	$Pt-Rh_{29}$.	Au_{33}.	Au_{40}.	Ag_{43}.	Pd_{46}.	Cu_{47}.
$\dfrac{0\cdot015}{1\cdot269}$	$\dfrac{0\cdot121}{6\cdot836}$	$\dfrac{0\cdot06}{3\cdot21}$	$\dfrac{0\cdot015}{0\cdot495}$	$\dfrac{0\cdot083}{2\cdot999}$	$\dfrac{0\cdot018}{1\cdot425}$	$\dfrac{0\cdot057}{1\cdot583}$	$\dfrac{0\cdot006}{1\cdot512}$
or $\dfrac{1}{84}$	$\dfrac{1}{57}$	$\dfrac{1}{53}$	$\dfrac{1}{33}$	$\dfrac{1}{36}$	$\dfrac{1}{79}$	$\dfrac{1}{28}$	$\dfrac{1}{252}$

Now these ratios are all much smaller than one-eighteenth, hence we infer that the curves have taken a more or less quick turn in the neighbourhood of the boiling point of hydrogen, or perhaps above it.

On Plate 10 the observed resistances are displayed graphically. For convenience I make seven groups, namely platinum, gold, silver, copper, palladium, magnetic metals, and alloys ; and in order to bring the characteristics of these groups into comparison, each metal is supposed to have the resistance of 30 ohms at the freezing point. This number was chosen to suit the scale—the intention being that, roughly, the " plot " of resistance and temperature should be a line equally inclined to the two axes of resistance and temperature. This has been accomplished by taking a centimetre to represent 20° C. in temperature, and 2 ohms in resistance. The diagram for each group has the reading at 0° C. placed $2\frac{1}{2}$ cm. higher than that of the group below it, in order to obviate confusion among so many approximately coincident lines. Attention paid to this will enable each group of curves to be clearly seen and compared with the others.

The first noticeable peculiarity is the close coincidence of the two silver curves. For them, Callendar's α's, the Ω's, and the ratios of the resistances at 0° to that at the boiling point of hydrogen are almost the same, although the δ's differ much. In like manner the Dickson constants for Ag_{43} are all in the same ratio (about 5 : 2) with those for Ag_{34}.

Next, the curves for P_7, Au_{40}, the two silver, and Pd_{46}, are very approximately parallel. Of the two palladiums, Pd_{35} would appear to have contained so much impurity as to have behaved almost like an alloy. The two alloys take up quite independent positions compared either with the purer metals, or with themselves, tending more to parallelism with the axis of temperature. In this connection I may mention that I constructed and used once or twice a carbon thermometer; in its case the resistance diminished as the temperature rose (a result already known), and its " plot " departed still farther from the pure metals than the alloys do, its α being − ·08048.

The magnetic metals present the most striking curves, being at first sight quite unlike any of the others. But on closer inspection we shall find that this is not so, and in fact they give the clue to the general connection between resistance and temperature in metals. The magnetic metals and gold were found to have *negative* values of δ. Now, if we examine the curves of the other metals, they will all be found concave towards the axis of temperature, for the arcs extending from the boiling point of water, through the freezing point, down to the boiling point of oxygen; while below the boiling point of oxygen these curves are convex to this axis. On the other hand, gold and the magnetic metals are already convex to this axis from the boiling point of water to the lowest temperature reached.

This leads me back to the research made by Professor Fleming and myself in 1896* on the electric resistance of mercury, in which we were able to observe the resistance of the metal from far below its melting point, and considerably above it when in the molten state. The curve connecting the resistance of mercury with temperature, throughout this range, including the change of state, was somewhat like the disused old English *f,* the temperature being measured horizontally to the right, and the resistance vertically upwards. In the present instance, though in different circumstances, this same curve reappears.

For platinum, silver, copper, palladium, and the alloys these experiments include a part of the curve (fig. 1) starting from (say) P, passing through I, the point of inflexion, and through Q down towards the absolute zero; whereas, in the case of gold and the magnetic metals, the corresponding part of the curve begins below I, (say) at Q, and proceeds thence towards the absolute zero. Professor Callendar, from former experiments of Professor Fleming and myself, had noticed this behaviour in the case of platinum.†

The eight observations below the boiling point of hydrogen are shown in Plate 10.

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* " On the Electric Resistivity of Pure Mercury at the Temperature of Liquid Air," ' Roy. Soc. Proc.,' vol. 60, p. 76.
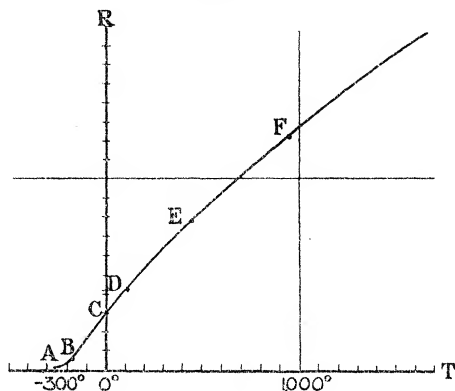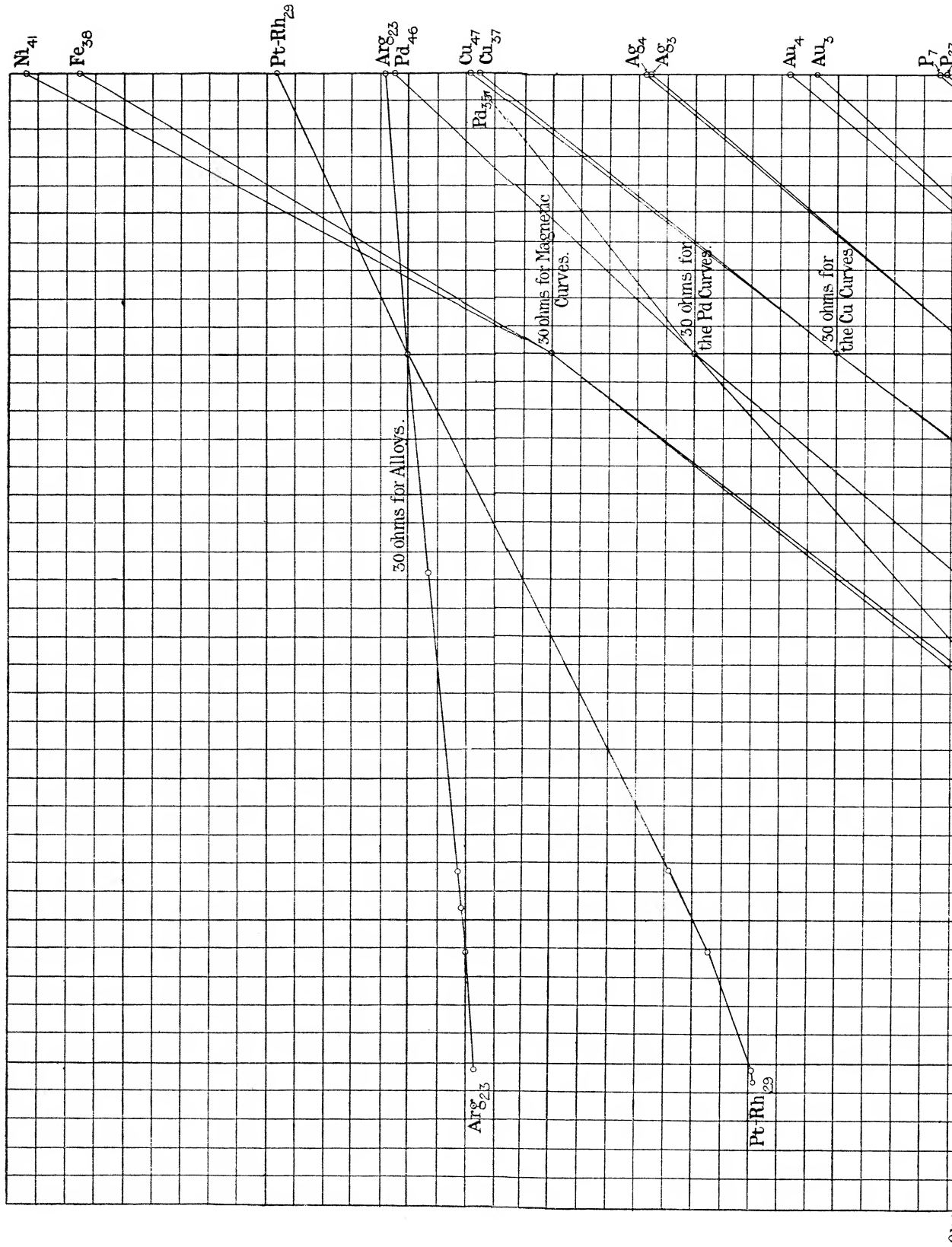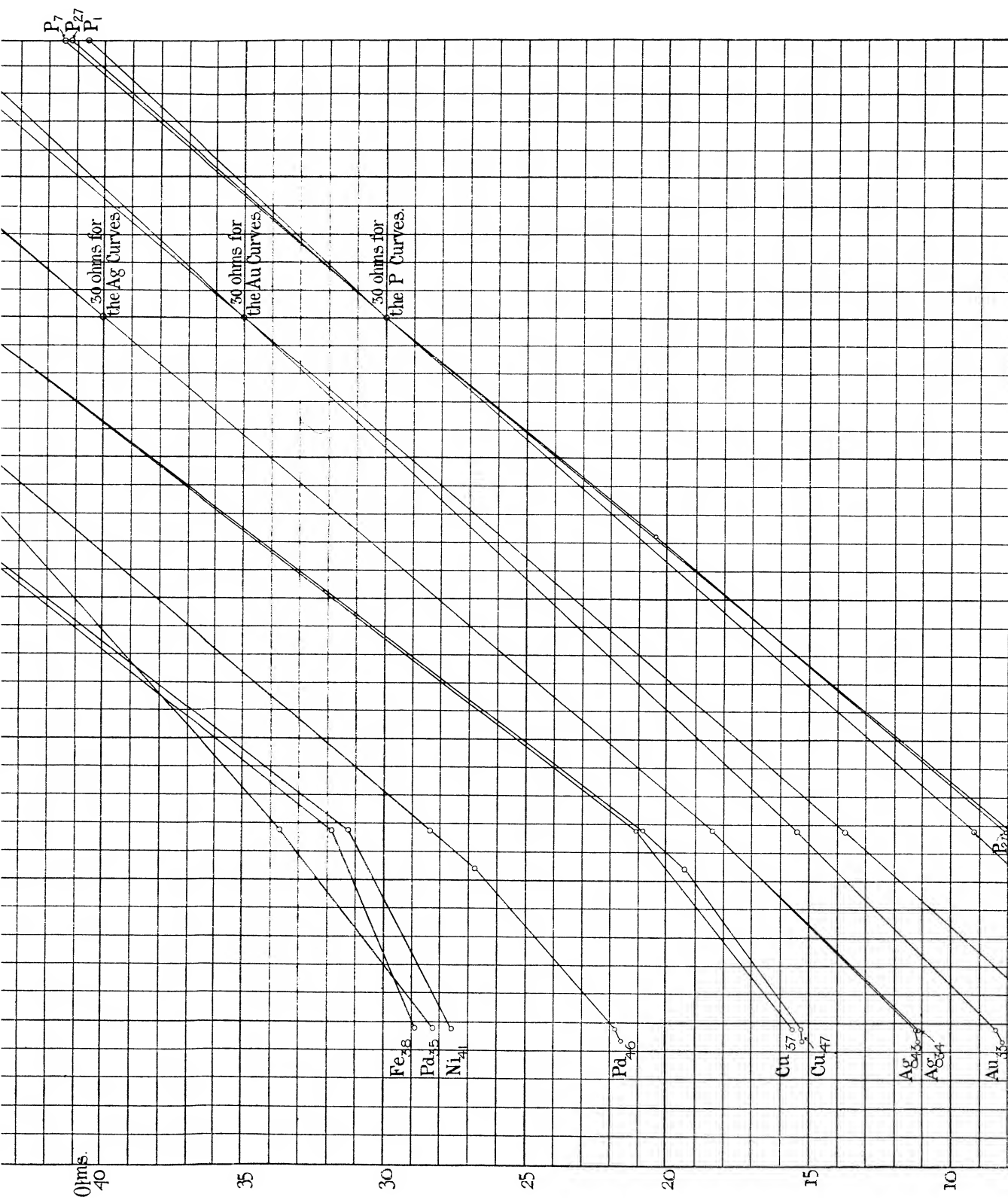
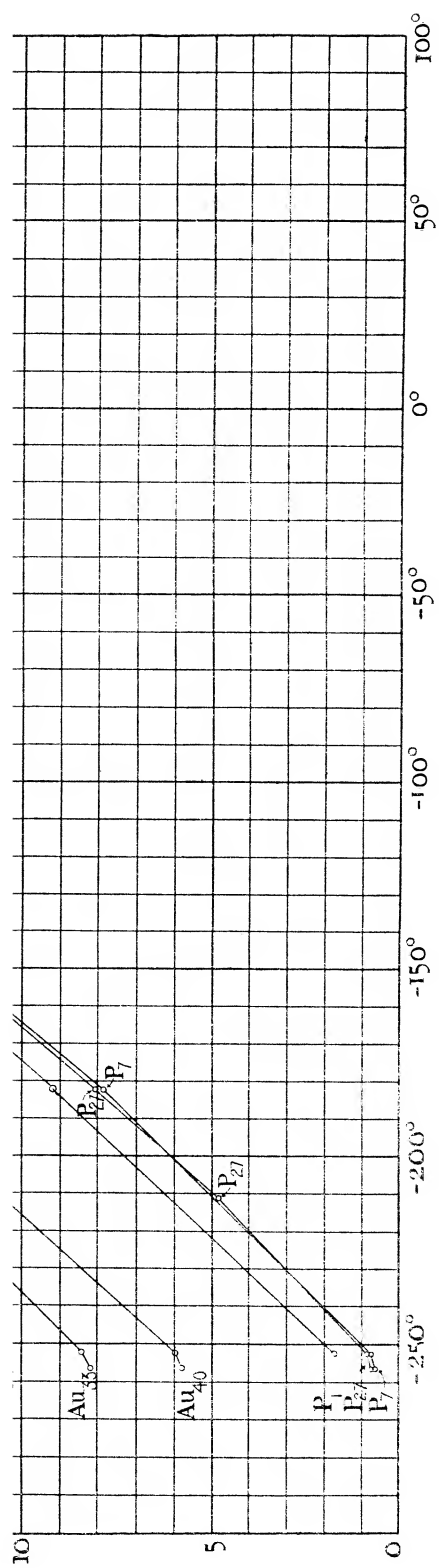† ' Phil. Mag.,' vol. 47, pp. 218, 222.

FIG. 1.
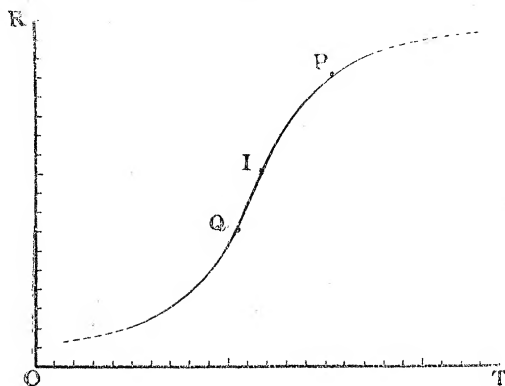
It is clear that in no case can anything parabolic connect resistances and temperatures ranging from the boiling point of water to that of hydrogen. Just as we seek for a circle of curvature at any point of a curve, so in the present case we may, at a point, or over a short range of the f, seek for an approximate parabola; but any such parabola will be of no, or little, use for extrapolation. I have mentioned that the value of δ for my platinum (Callendar) parabola is about 2·5, whereas observers at high temperatures finds its value about 1·5 for pure platinum. Such differences have been found by others also, but they do not seem to have attracted attention. On looking at fig. 2, we shall find the discrepancy easily accounted for. The portion ABCD of the curve represents roughly (on a much reduced scale, in order to show the curvature more clearly) the curve of P_{27}, given in Plate 1. The points B, D, E, represent the boiling points of oxygen, water, and sulphur; and C, F, represent the freezing points of water and silver.

FIG. 2.

Dewar.

Ni₄₁

Fe₃₈

Pt-Rh₂₉

Arg₂₃
Pd₄₆

Cu₄₇
Cu₃₇

Pd₃₅

Ag₅₄
Ag₅

Au₄
Au₅

P₇
P₇₇

30 ohms for Alloys.

30 ohms for Magnetic Curves.

30 ohms for the Pd Curves.

30 ohms for the Cu Curves.

Arg₂₃

Pt-Rh₂₉

If parabolas with vertical axes (Callendar) be described through the points (1) B, C, D; (2) C, D, E; (3) C, D, F, they will be different, since the curve of observation is not itself parabolic. In the case of these parabolas, where the resistances at C and D are common to all, the product of δ and the parameter (P) of the corresponding parabola is constant; hence the smaller δ becomes, the more open—or less curved—will be the parabola along the arc we have to deal with. This result is in accordance with the curve in fig. 2, and explains why, as I have already pointed out, the two parabolas for high and low temperatures are not only different, but also may differ from each other by any amount, within certain limits depending on the nature of the unknown curve of temperature and resistance.

I am greatly indebted to Mr. J. D. H. Dickson, M.A., Fellow of Peterhouse, for help in the calculation and reduction of the observations.

" Physical Constants at Low Temperatures. (1)—The Densities of Solid Oxygen, Nitrogen, Hydrogen, etc." By Professor JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S. Received March 9, —Read March 17, 1904.

1. The following experiments on the solid densities of oxygen, nitrogen and hydrogen were carried out as part of a former investigation dealing with gaseous densities at low temperatures.*

The method adopted was to measure the volumes of the gases sucked into a cooled space of known capacity, when the temperature was such as in the first place to induce liquefaction and finally solidification. For such experiments to be successful the rate of liquefaction and the cooling must be under thorough control, otherwise the cooled space may not get completely filled with solid. Further, the volume of gas condensed ought to be as large as possible, in any case about 20 litres, in order to diminish errors inseparable from the mode of manipulation. The inertia of the bell-jars of the large gas-holders causes some variation in the pressure; and errors of their calibration, and want of uniformity of temperature in the mass of gas, are all important factors. As my object was to ascertain experimentally the limiting density in the solid state, the elimination of these variations was not so important as it would have been for the study of fluid density.

The dry purified gas was contained in a gas-holder connected by a pipe with a glass bulb of 20 or 30 c.c. capacity, sealed to a narrow tube some 10 cm. long, with a glass stop-cock at the end. The

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* " The Specific Volumes of Oxygen and Nitrogen Vapour at the Boiling Point of Oxygen," ' Roy. Soc. Proc.,' vol. 69.